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Applying Separations Science to Waste Problems

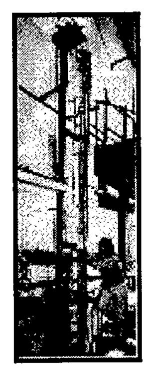
Separation of Ultrafine Particles from Waste

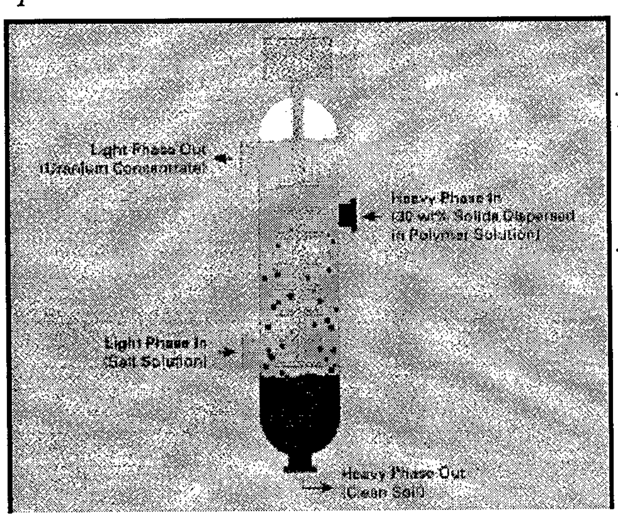
The Chemical Technology Division, recognized worldwide for its expertise in separations science, specializes in developing innovative processes for treating contaminated soils, wastewater, solid nuclear wastes, and other liquid and solid waste.

One such process involves grinding of solid waste to an average particle size of about one micrometer, followed by selective partitioning of the ultrafine particles between two immiscible aqueous phases. This aqueous biphasic separation process will recover most of the contaminants in a concentrate that has a volume of only a few percent of the initial waste volume.

An application of this process being investigated involves recovery or concentration of refractory materials from incinerator ash, ash heels, and metallurgical processing residues. Also under investigation are removal and concentration of uranium from contaminated soils at the DOE Fernald site in Ohio and selective partitioning of radionuclides from the caustic supernate in the high-level waste storage tanks at the DOE Hanford site.

Pilot plant developed for cleaning uranium-contaminated soil by aqueous biphasic separation.





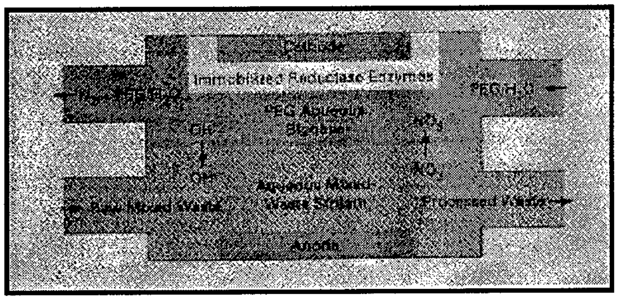
Schematic of aqueous biphasic separation for uranium-contaminated soil. This partitions ultrafine uranium particles to an aqueous salt phase and the cleaned soil to a water-soluble polymer. The water-soluble polymers used in biphase formation are inexpensive, nontoxic, and biodegradable.

Biocatalytic Destruction of Nitrate and Nitrite

Many of the aqueous wastes that have accumulated

from DOE defense operations have high nitrate and nitrite concentrations, which present a disposal problem. For example, if treated by high-temperature vitrification, these wastes will generate significant quantities of nitrogen oxides and can become chemically unstable and potentially explosive. The disposal problem would be minimized if the nitrate and nitrite in the waste were destroyed before preparation of the final waste form. We are thus developing a process that combines aqueous biphasic separation with immobilized enzymes for reducing nitrate and nitrite to innocuous products, namely, elemental nitrogen and water.

Although this process is being developed for defense waste streams, it also has application to other nitrate-containing streams in the industrial sector, such as chemical plant discharge and drinking water.



Schematic of biocatalytic reactor for destroying nitrate. The process combines immobilized enzyme technology with aqueous biphasic separation. A key part of the process is the partitioning of the nitrate into a polyethylene glycol (PEG) aqueous phase before enzymatic reduction. This allows the enzymes to be isolated from the harsh environment of the aqueous waste streams.

Electrometallurgical Treatment of Spent Nuclear Fuel

Researchers in the Division have developed <u>a compact, efficient method</u> for conditioning spent nuclear fuel for disposal. The method, known as electrometallurgical treatment, separates fission products and transuranic elements from the larger quantity of uranium present in spent fuel. The pure uranium product can be stored, recycled, or converted to an oxide for disposal as a low-level waste. The fission products and transuranic elements are immobilized in highly stable waste forms. Compared with conventional reprocessing technologies, the electrometallurgical technology holds promise for significantly reduced costs, decreased volumes of high-level radioactive waste, and negligible volumes of secondary or low-level wastes. The method could facilitate the timely and environmentally sound processing of most of the nearly 3000 tons of spent nuclear fuel accumulated within the DOE complex.

The expertise in high-temperature thermodynamics, fluid handling, and containment materials resulting from CMT's past work on electrometallurgical technology is applicable to numerous areas, both nuclear and non-nuclear. These areas include the extraction of plutonium from actinide-bearing waste that has been generated in defense programs, treatment of enrichment tailings from nuclear plants, and low-cost production of lanthanides useful to the metals industry.

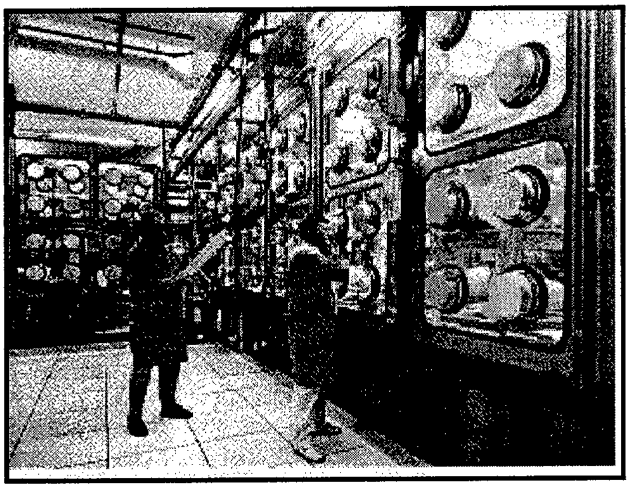
Uranium deposited on cathode by electrometallurgical treatment of spent nuclear fuel.

Waste Forms for Electrometallurgical Treatment

Operations during electro-metallurgical treatment will result in two waste streams: a metal stream consisting of fission products and cladding hulls from the spent fuel, and a salt stream that contains

fission products and transuranics. We have developed processes for treating and packaging these waste streams. The metal waste stream is handled by a melting step that removes the transuranic elements and produces a high-level waste form. The salt waste stream is passed through a zeolite bed that absorbs the transuranics and fission products. The zeolite loaded with fission products is hot pressed with a glass frit to produce a second high-level waste form. Both the mineral waste form and the metal waste form are stable under envisioned repository conditions and are highly resistant to leaching of waste elements. Large glovebox facilities have been built in CMT for carrying out experiments with zeolite and metal waste forms, as well as other radioactive materials and processes that must take place in a protected atmosphere.

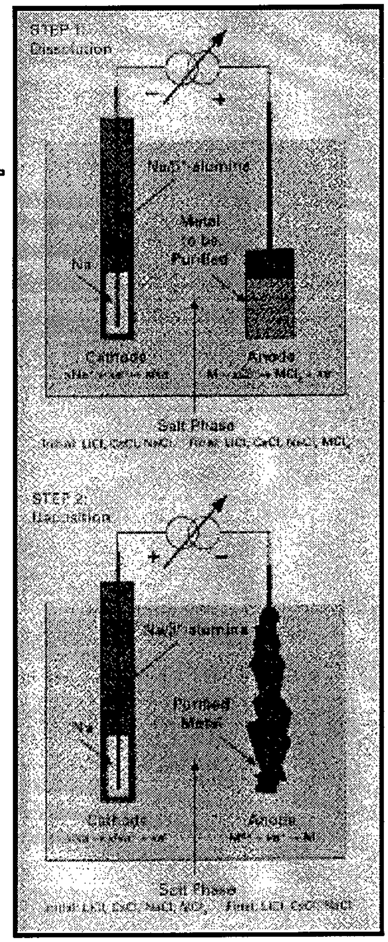
The technology resulting from this work could also be applied to waste streams from production of special nuclear materials, nonradioactive toxic wastes such as barium-contaminated salts from industrial processes, and industrial wastes bearing contaminants such as heavy metals.



Extensive glovebox facilities built in CMT for conducting experiments with radioactive wastes.

Ion Replacement Electrorefining of Metals and Molten Salts

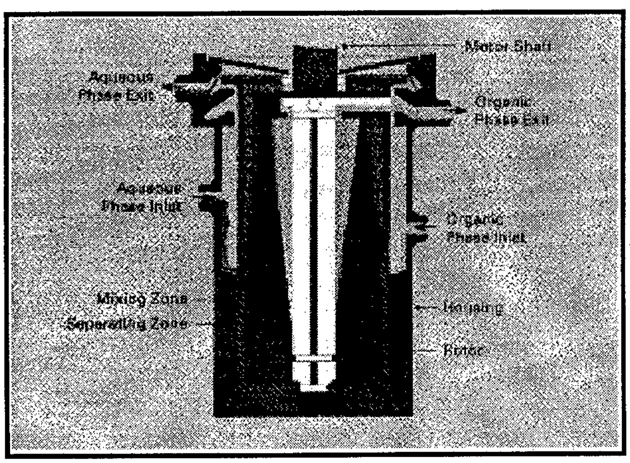
We have invented several new metal separation and purification processes as a result of past work on treating spent reactor fuel. One such process, called ion replacement electrorefining, overcomes the shortcomings of conventional electrorefining and electrowinning and could lead to improved processing capabilities for purifying a variety of metals and recovering oxidized metals from molten salts. It uses liquid sodium contained in a b-alumina tube as a cathode during metal dissolution in a molten salt electrolyte, then as an anode during metal separation and deposition on inert cathodes. One application of this process is separating transuranic elements from fission products that occur in typical radioactive waste forms generated by commercial nuclear reactors and by defense nuclear programs. The b-alumina/sodium electrode also has potential as a reliable reference electrode for use in molten salts. Such an electrode, when combined with electroanalytical methods such as potentiometric and voltammetric analysis, could yield better sensors for monitoring and controlling industrial high-temperature processes.



Schematic of ion replacement electrorefining for purifying metals. The metal to be purified is first dissolved in a molten salt, then deposited in pure form on an inert cathode.

Centrifugal Contactor for Processing Liquid Radioactive Waste

We have developed an annular centrifugal contactor for use in liquid/liquid solvent extraction. Our primary goal has been to quickly and efficiently recover transuranic elements and fission products from liquid radioactive waste. The CMT-designed centrifugal contactor has several advantages over other solvent-extraction equipment currently in use. It requires less solvent, is easily modified to handle different solvent compositions, can be remotely operated and maintained, and has low construction and operating costs. Also, its high extraction efficiencies (above 99%) and low solvent holdup allow a pilot-scale unit to attain steady state with less than a liter of feed. Because of these advantages, the contactor has become the standard for performing solvent extraction in the DOE community. Units have been operated at Argonne, Westinghouse Hanford, Pacific Northwest Laboratory, Los Alamos National Laboratory, Westinghouse Idaho, Rocky Flats Plant, Y-12 Plant, Savannah River Site, and Oak Ridge National Laboratory. The benefits that make the centrifugal contactor the equipment of choice in the nuclear industry would be of value for waste treatment in the pharmaceutical, biotechnology, and metallurgical industries. In a related effort, a computer model has been developed to design flowsheets for implementing solvent extraction processes with centrifugal contactors as well as mixer settlers and pulsed columns.



Schematic of a single centrifugal contactor used for solvent extraction. The aqueous waste enters the contactor and is mixed with an organic solvent, which extracts the contaminant. The two liquids are then separated by centrifugal force inside the rotor. Multiple contactors are connected in series to run a flowsheet

Glassy Waste Forms

Glasses are a candidate waste form being considered for disposing of radioactive and hazardous wastes. The CMT Division has more than 15 years experience in preparing glass forms containing nuclear waste materials and evaluating their performance under simulated repository conditions. This expertise is now being applied to the vitrification of DOE wastes with relatively low levels of radioactive and hazardous elements. A new vitrification method, developed in CMT, blends several waste streams to minimize the amounts of glass-forming additives necessary and thereby reduce costs. This method produces a stable glass waste form of minimum volume. A similar method is also being explored for producing a glass-crystalline composite for handling waste streams that are difficult to vitrify. Product durability is evaluated by using test methods developed for high-level nuclear waste and adapted for use with other kinds of waste.

Micrograph of nuclear waste glass reacted with water. As the glass reacts, actinides (blue areas) are released to solution as colloidal particles. The results are used in modeling of glass durability.

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